Epitaxial Growth of GaN on Silicon Using Molecular Beam Epitaxy and Its Application for MEMS Based Hydrogen Gas Sensor

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URL	http://hdl.handle.net/10097/62717

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授　与　学　位	博士（工学）
学位授与年月日	平成２６年９月２４日
学位授与の根拠法規	学位規則第４条第１項
研究科，専攻の名称	東北大学大学院工学研究科（博士課程）ナノメカニクス専攻
学位論文題目	Epitaxial Growth of GaN on Silicon Using Molecular Beam Epitaxy and Its Application for MEMS Based Hydrogen Gas Sensor（分子線エピタキシーを用いたシリコン上 GaN のエピタキシャル成長と MEMS 型水素ガスセンサーへの応用）
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論 文 内 容 要 旨

Hydrogen (H_2) sensor is one of the most important factors that affect the development of the green and renewable H_2 energy. Both the Mazda and Honda manufactured hydrogen fuel automobiles in 2006, the Mazda RX-8 Hydrogen RE and the Honda FCX Concept, respectively, creating a new era of H_2 energy usage in our daily life. For the development of hydrogen fuel automobiles, H_2 sensors that are capable to operate in harsh environment, such as high temperature and corrosive conditions, are required to monitor the automotive exhaust, the engine, and the leakage. But H_2 sensor suitable for harsh environment is lacked.

Recently, the wide band gap GaN semiconductor has attracted much attention for H_2 detection since it is capable to operate at high temperature of 400°C while the most widely used silicon semiconductor is limited to 150 °C. Moreover, the GaN is also highly inert to most corrosive chemicals. The current research on the GaN film, nevertheless, exhibits high limit of detection (LOD_{H2}), long response time τ, and high power energy consumption. The GaN nanostructure is regarded as a promising approach to enhance the H_2 detection performance. The current researched GaN nanostructures, such as the nanowire and the nanocolumn, are separated nanostructures, which are of great difficulty to fabricate to electrical devices. From the aspect of commercialization, the GaN nanostructure should be easy to process. Therefore, it is of great importance to develop an easy-processable GaN nanostructure and investigate its H_2 detection performance. In addition, with the development of wireless sensor network, a highly compact monolithic H_2 sensor with small size, low power consumption, and mass production is highly desired.

This work mainly focuses on the growth of a novel GaN nanostructure namely the honeycomb GaN nanostructure and on the investigation of the H_2 sensor based on the novel GaN nanostructure. Moreover, a highly compact monolithic H_2 sensor was proposed and developed using the micro-electro-mechanical systems (MEMS) technology.

Shivaprasad *et al* firstly discovered the epitaxial growth of a honeycomb GaN nanonetwork on the sapphire (Al_2O_3) substrate. Almost at the same time, I epitaxially grew a honeycomb GaN nanostructure on the Si (111) substrate, which is compatible with the mature Si micromachining technology. Under N_2 rich growth condition, GaN was grown in 3-dimentional mode to the honeycomb GaN nanonetwork using molecular beam epitaxy (MBE) in chapter 2. Different from the separated GaN nanowire, the honeycomb GaN nanonetwork is continuous in the lateral direction, making it in-plane electrically conductive, which is of great importance for electrical device fabrication. The surface area to volume ratio (SA/V) is 0.034 nm^{-1}, 17 times larger than the GaN film. X-ray diffraction (XRD) pattern was measured, indicating hexagonal GaN with high *C* axis orientation. The full width at half maximum (FWHM) of the rocking curve is 48 arc min, suggesting high crystallinity. Basing on the lattice constants a=3.193 and c=5.182 Å measured from the XRD result, the stress inside the honeycomb GaN nanonetwork was calculated. The in-plane stress σ_x and out-plane stress σ_z of the honeycomb GaN nanonetwork were evaluated, 0.55 and 0.22 GPa, respectively. In comparison with the GaN film, the stress of the nanonetwork is one order smaller. Photoluminescence measurement was also carried out, exhibiting strong near-band-edage emission at 364.8 nm, which indicates high optical quality. Moreover, the polarity was evaluated using chemical etching, suggesting the Ga-polar GaN growth on the Al-polar AlN buffer layer. Similar to the GaN nanowire, the honeycomb GaN nanonetwork is free of dislocation according to the transmission electron microscopy (TEM) measurement. Through adjusting the N/Ga ratio, the size of GaN nanowall can be controlled ranging from 30 nm to 200 nm. Because of its high quality and large SA/V as well as in-plane electrical conduction, therefore, the novel honeycomb GaN nanonetwork is promising for nano H_2 sensors.

On the honeycomb GaN nanonetwork, a Pt/GaN Schottky didoe type nano H_2 sensor was fabricated and investigated in chapter 3. When the Pt/GaN Schottky didoe is exposed to H_2 gas, the Schottky contact Pt dissociates the H_2 molecule to H atoms. Some of these H atoms are absorbed in the Pt/GaN interface and change to the H dipoles, resulting in the decrease of the Schottky barrier, basing on which the H_2 gas is detected. From the SEM images and current-voltage (*I-V)* measurements, the Pt/ honeycomb GaN nanonetwork Schottky diode could be regarded as one H_2 sensor element comprised of nano-Schottky diodes in parallel. The barrier height and ideality factor for the nano Schottky diode are 0.497 eV and 38.5, respectively. A columnar model with metal core and semiconductor shell was proposed for the one-dimensional nano Schottky diode on the honeycomb GaN nanonetwork. The dependences of the electric field and the barrier width on the nano Schottky diode size "*a"* were investigated by solving the *Poisson* equation and the *Gauss*'s *law*. From this model, it is observed that when the size "*a"* >l_c *(characteristic length)*, the Schottky diode is independent of the size "*a"* and it is regarded as a "large" Schottky diode. On the other hand, when the size "*a"* < l_c, both the barrier width *w* and electric field are profoundly affected by the size "*a"*. For the GaN with carrier concentration of 8×10^{16} cm^{-3}, the l_c is 77 nm. This Schottky diode on honeycomb GaN nanonetwork is able to perform well at room temperature in detecting hydrogen gas with concentrations from 320 to 10,000 ppm. Because of its in-plane electrical conductivity, a two-mask process without any nanofabrication equipment is enough for the fabrication of the H_2 nano-sensors on the honeycomb GaN nanonetwork, which is as easy as that on a GaN film.

In order to better investigate the H_2 sensors on the honeycomb GaN nanonetwork, comparative study of the H_2 sensors on the honeycomb GaN nanonetwork grown by MBE and on the planar GaN film grown by Metal Organic Chemical Vapor Deposition (MOCVD) was carried out. The Pt/planar GaN film Schottky diode was well fabricated with Schottky barrier Φ_b of 0.53 eV and ideality factor n of 3.03. In 1% H_2 gas, the Schottky barrier decreased to be 0.43 eV. The H_2 sensor on the planar GaN film shows response time τ of 80 s (10,000 ppm) and 2,000 ppm limit of detection for hydrogen gas (LOD_{H2}) at 373 K. For the Schottky diode on the honeycomb GaN nanonetwork, the Schottky barrier heights Φ_b in air and in 1% H_2 were 0.497 and 0.454 eV, respectively. A significant improvement in H_2 detection is observed. The characteristics of the H_2 sensor on the honeycomb GaN nanonetwork were quantitatively studied in comparison with that on the planar GaN film. The response time τ is shortened by a factor of 27 (3 s *versus* 80 s). In particular, the LOD_{H2} is lowered by two orders of magnitude, from 2,000 to 50 ppm. Moreover, the operating temperature could be reduced to room temperature. The 50 nm thick Pt Schottky contact deposited on the honeycomb GaN nanonetwork is a nanonetwork with SA/V of about 0. 1 nm^{-1}, five times larger than that of the Pt film on the planar GaN film (0.02 nm^{-1}) with the same thickness. The lower LOD_{H2} of 50 ppm is attributed to the larger SA/V. H_2 sensing performance at 303, 340 and 373K were measured to evaluate the H_2 sensor activation energy E_a. Through analyzing the transient-state, the activation energies E_a for the H_2 sensors on the planar GaN film and on the honeycomb GaN nanonetwork were evaluated, 6.22 and 2.4 kcal/mol, respectively. The reduced activation energy E_a from 6.22 to 2.4 kcal/mol is regarded as the reason that leads to the superior H_2 detection of the honeycomb GaN nanonetwork in terms of response time τ and operating temperature. The significant reduction of the activation energy E_a for the nano H_2 sensor is applicable to explain the general phenomenon that the operating temperature of the H_2 sensors on various nano materials could be lowered to room temperature while their corresponding planar films require an elevated operating temperature. Through analyzing the steady-state, the relationship between H_2 concentration and V_{output} was developed. Because of its superior performance as well as easy fabrication, it is possible that the nano H_2 sensors on the honeycomb GaN nanonetwork could operate for real world applications to detect low H_2 concentration at a wide operating temperature range.

In addition to the popular three “S” namely stability, sensitivity, and selectivity, H_2 sensors with low power consumption, mass production, and small size are desired to meet the demands of a future H_2 economy. In chapter 5, a monolithic H_2 sensor on the honeycomb GaN nanonetwork was proposed and fabricated basing on the MEMS technology. Because an elevated temperature is needed for hydrogen sensing, typically 100 to 200°C, a Pt resistor was introduced as a micro-heater. To improve the reliability, a reference sensor is usually needed to compensate the environment fluctuations, such as the temperature and the moisture fluctuations. Since it is difficult to seal a Pt/GaN Schottky diode and use it as a reference sensor, here, an Au/GaN Schottky diode was employed as the reference sensor. Therefore, a Pt/GaN Schottky diode H_2 sensor, an Au/GaN Schottky diode reference sensor, a Pt micro-heater and a resistive temperature detector (RTD) were integrated in the monolithic H_2 sensor. The H_2 sensor and the reference sensor were arranged in a wheat-stone bridge. In this work, two types of Pt resistor with different designs, namely type I and type II were designed and studied. To reduce the heat conduction through Si substrate, the beneath Si was etched by inductive coupled plasma reactive ion etching (ICP-RIE), generating a suspended honeycomb GaN nanonetwork. The Pt micro-heater on the suspended GaN has high heat efficiency. To elevate the monolithic sensor to the typical operating temperature of 200°C, the power consumptions for type I and type II are 63 mW and 21 mW, respectively. Considering the suggested power consumption of < 100 mW for the H_2 sensor, both designs can meet this low power consumption requirement. The heating time and the cooling time for the micro-heater (between 419°C and 43°C) are short, 2.3 ms and 2.5 ms, respectively. At the same time, the resistance of the Pt resistor has a strong linear dependence on the temperature in the range from -200°C to 600°C, basing on which it is used as a well-known RTD. In this monolithic H_2 sensor, thus, the Pt resistor is employed as both a micro-heater and a RTD. The temperature coefficient of resistance (TCR) was evaluated to be 19.11×10^{-4}/°C. Moreover, the feasibility of the Au/GaN Schottky diode as a reference sensor was evaluated. As a reference sensor the Au/GaN Schottky diode should be low sensitive to the H_2 gas and effective to compensate the environment fluctuations. After exposing to the same H_2 concentration, the reference sensor has low sensitivity to the H_2 gas, about 1/15 of the H_2 sensor. In the temperature fluctuation test, the reference sensor could suppress the temperature fluctuation effect to 1/5. Therefore, it is feasible to employ the Au/GaN Schottky diode as a reference H_2 sensor. For this monolithic H_2 sensor integrated with a reference sensor, a micro-heater and a RTD, the overall size is 2mm × 3mm. In addition, basing on the MEMS technology the monolithic H_2 sensor is mass productive. On a 2cm × 2cm chip, there are 32 monolithic H_2 sensor arrays. Therefore, on the honeycomb GaN nanonetwork, a low power consumption, small size, and mass productive monolithic H_2 sensor was obtained using MEMS technology.

論文審査結果の要旨

窒化ガリウムは発光素子および電子回路素子として実用化および研究開発が進められているが，耐熱性，耐腐食性などを特徴とする半導体センサー材料としても応用が期待されている。水素ガスは次世代のクリーンエネルギーとして燃料電池自動車などへの利用が進められているが，爆発を起こす濃度範囲が広いなど危険性が高いので，ガス漏れ検知センサーを備えることが安全を確保するために不可欠となっている．窒化ガリウムは，高温などの苛酷環境の新しい半導体水素ガスセンサー材料として利用が期待されているが，測定感度および応答速度が十分でなく，実用化を阻む要因となっている。本研究では，シリコン基板上に窒化ガリウムのネットワーク状結晶を分子線エピタキシー法により成長し，高い表面積/体積比率とネットワーク構造による通電性を利用し，窒化ガリウム半導体水素ガスセンサーの感度と応答特性を改善している。本論文は，これらの研究成果をまとめたものであり，全編6章からなる。

第1章は緒論であり，本研究の背景，目的および構成を述べている。

第2章では，シリコン基板上へ窒化ガリウムのネットワーク状結晶を成長させた結果と結晶特性の評価について述べている。窒素供給が豊富な条件で窒素/ガリウムの比を調節し，幅30nmから200nmの窒化ガリウムのナノウォール結晶がハニカム状に連結したネットワーク結晶を成長できることを見出している。これらは有益な成果である。

第3章では，窒化ガリウムのネットワーク状結晶上に形成したショットキーダイオード型水素センサーの製作と特性について述べている。ナノウォール結晶上のショットキーダイオードの解析のためコラム状ショットキーダイオードモデルを提案し，特性を説明している。センサーの特性として，室温で320ppmから10,000ppmの濃度において，水素ガスを検出できることを報告している。これらは有用な知見である。

第4章では，分子線エピタキシー法で成長した窒化ガリウムのネットワーク状結晶と有機金属気相成長法により成長した窒化ガリウムの平坦な薄膜結晶のショットキーダイオード型水素センサーの比較研究について述べている。温度373Kで濃度10,000ppmの場合，応答時間はそれぞれ3秒と80秒であり，検出限界はそれぞれ50ppmと2000ppmであることより，ネットワーク状結晶のセンサー特性が優れていることを示している。これらの改善は，ネットワーク状結晶の活性化エネルギーが，平坦な結晶の場合の値6.22kcal/molに比較して，2.4kcal/molに低減されたことによる。これらの結果は高く評価できる。

第5章では，マイクロマシニング技術により，窒化ガリウムのネットワーク状結晶を用いて，実用的な水素センサーを製作し，特性を測定した結果について述べている。シリコン上に成長したネットワーク状結晶上に，白金/窒化ガリウムショットキーダイオードを水素センサーとして形成し，金/窒化ガリウムショットキーダイオードを参照用センサーとして形成している。また，白金ヒータと白金抵抗温度センサーも同時にを組み込み，シリコン基板のエッチングによる自立膜構造を形成することで熱絶縁している。このようにモノリシックに製作したセンサーの全体の大きさは2mm×3mmであり，水素ガスセンサーとしての動作を確認できている。これらは有益な成果である。

第6章は結論である。

以上要するに本論文は，分子線エピタキシー法によりシリコン基板上に窒化ガリウムのネットワーク状結晶を成長し，水素ガスセンサーへの応用を提案したもので，ナノメカニクスおよびセンサー工学の発展に寄与するところが少なくない。

よって，本論文は博士(工学)の学位論文として合格と認める。